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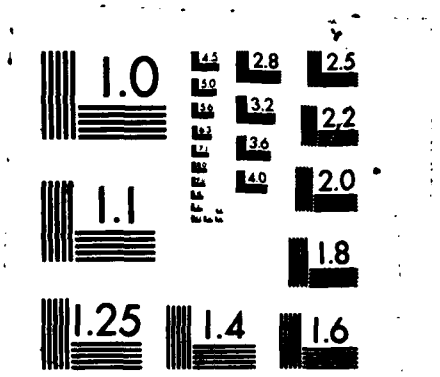

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# SILICIDE/SI INTERFACES IN VLSI STRUCTURES

Final Technical Report

1 May 1984 to 30 September 1986

ONR Contract: N00014-84-K-0342

Cornell No. ONR: E74-8424



Submitted to

Office of Naval Research

(L. Cooper)

Short Title: "Interfaces"

Principal Investigator:

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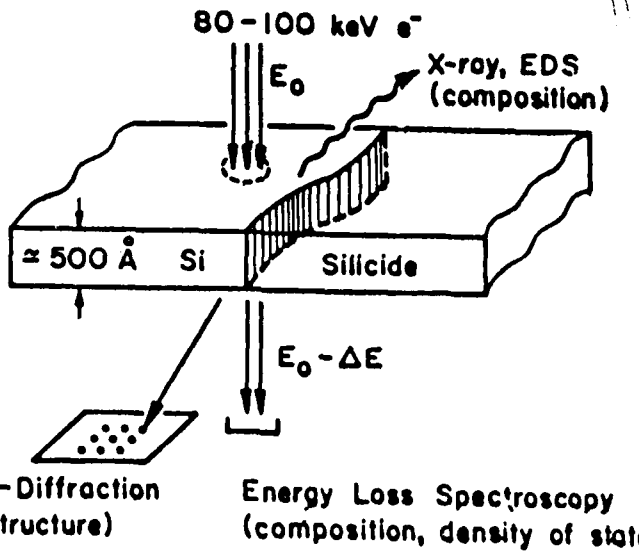
15 June 1987

## Abstract

The stated objective of this program was to investigate Silicide/Si interfaces using electron energy loss spectroscopy, electron micro-diffraction and electron induced x-ray emission with fine-focussed electron beams, as illustrated below. We achieved the major objectives of the program and two students received PhD's (Barbour and Kavanagh) with support from this program. There were 15 refereed publications that acknowledged support from ONR in journals including Applied Physics Letters, Journal of Applied Physics and Physics Review Letters.

For silicide studies we used self-supporting lateral diffusion couples because thin samples are needed to minimize electron-beam and maximize spatial resolution. In Ni-silicide structures, high resolution measurements were made of composition, structure and interface width; the compositional width of the ~~$Ni_2Si$-NiSi~~ interface boundary is at most 10nm.

The successful application of these techniques allowed us to investigate other technologically important interfaces: amorphous alloys, Poly Si/Si and GaAs/GaInAs interfaces. In the latter case, electron energy loss measurements using a scanning transmission electron microscope allowed identification of electronic states associated with a single misfit dislocation.



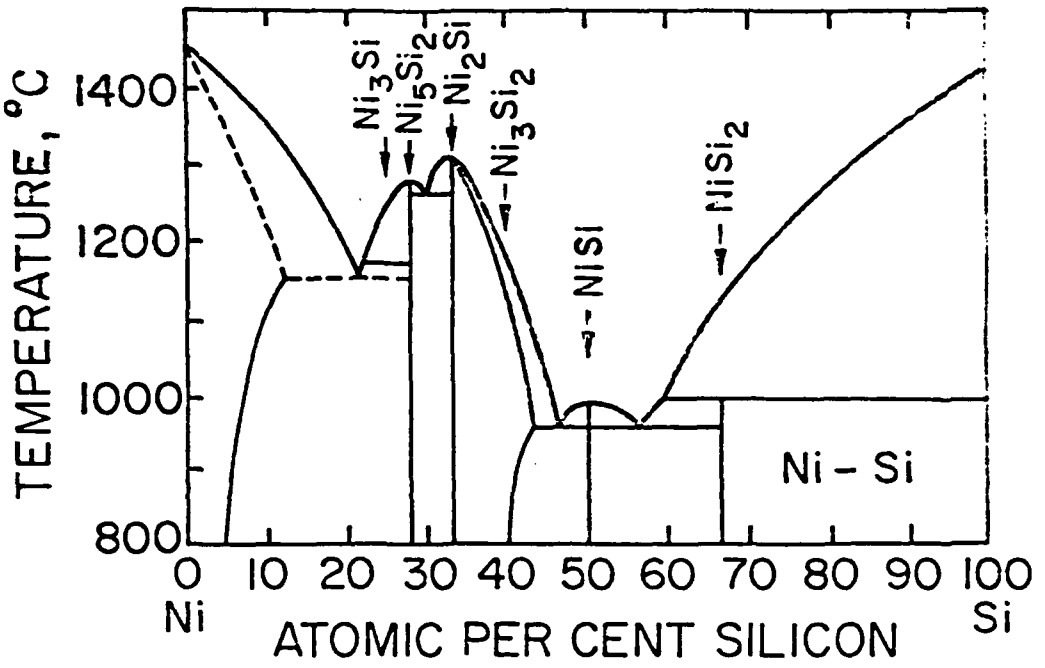
## I. Introduction.

The objective of this study was to carry out high spatial resolution studies of compostion gradients across silicides interfaces. We developed self-supporting lateral silicide diffusion couples to carry out these studies. Consequently one of the requirements of this program was to show that the behavior of lateral silicide diffusion couples could be related to the more conventional studies of silicide formation.

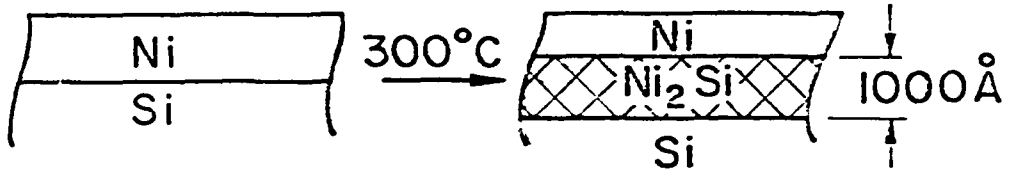
An overview of nickel silicide formation is given in figure 1. The equilibrium phase diagram shows the existence of 6 silicide phases all with melting points above 900°C. In conventional thin film silicide studies, a Ni layer is deposited on a single crystal substrate. Thermal annealing at temperatures around 300°C results in the formation of a single phase $Ni_2Si$. The growth kinetics of this phase has been studied in detail with Rutherford backscattering spectrometry and phase identification provided by x-ray and electron diffraction. The general behavior by annealing deposited metal films on silicon is now well-characterized. At the other extreme, bulk diffusion couples have been formed by joining thick metal and Si layers and annealing to high temperatures so that bulk cross-sections can be obtained. In these bulk samples the entire phase sequence can be found as shown schematically in the lower portion of figure 1.

The two structures, thin-film and bulk, clearly differ from each other and we developed lateral diffusion couples to understand the difference in behavior. As shown in the upper portion of figure 2, a lateral diffusion couple is formed by depositing Ni islands (for example) on thin Si films. The Ni islands provide a Ni-rich source for subsequent diffusion of the Ni into the Si layer and the formation of silicide layers. Thermal annealing at 500°C leads to the formation of a sequence of silicide phases.

Prior to the start of the present program, we had used scanning electron microscopy (SEM) and electron microprobe measurements to determine the widths




1) In Thin Films — one phase dominates




2) In Bulk Samples — all phases

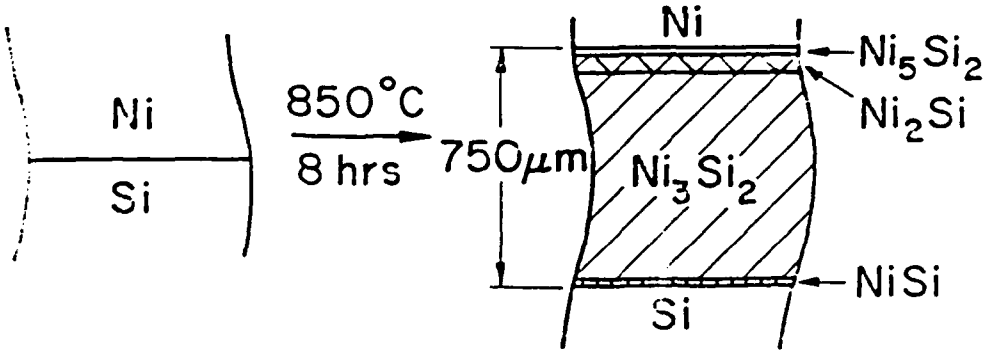



Fig. 1. Ni-Si equilibrium phase diagram and silicide formation in thin film and bulk samples.

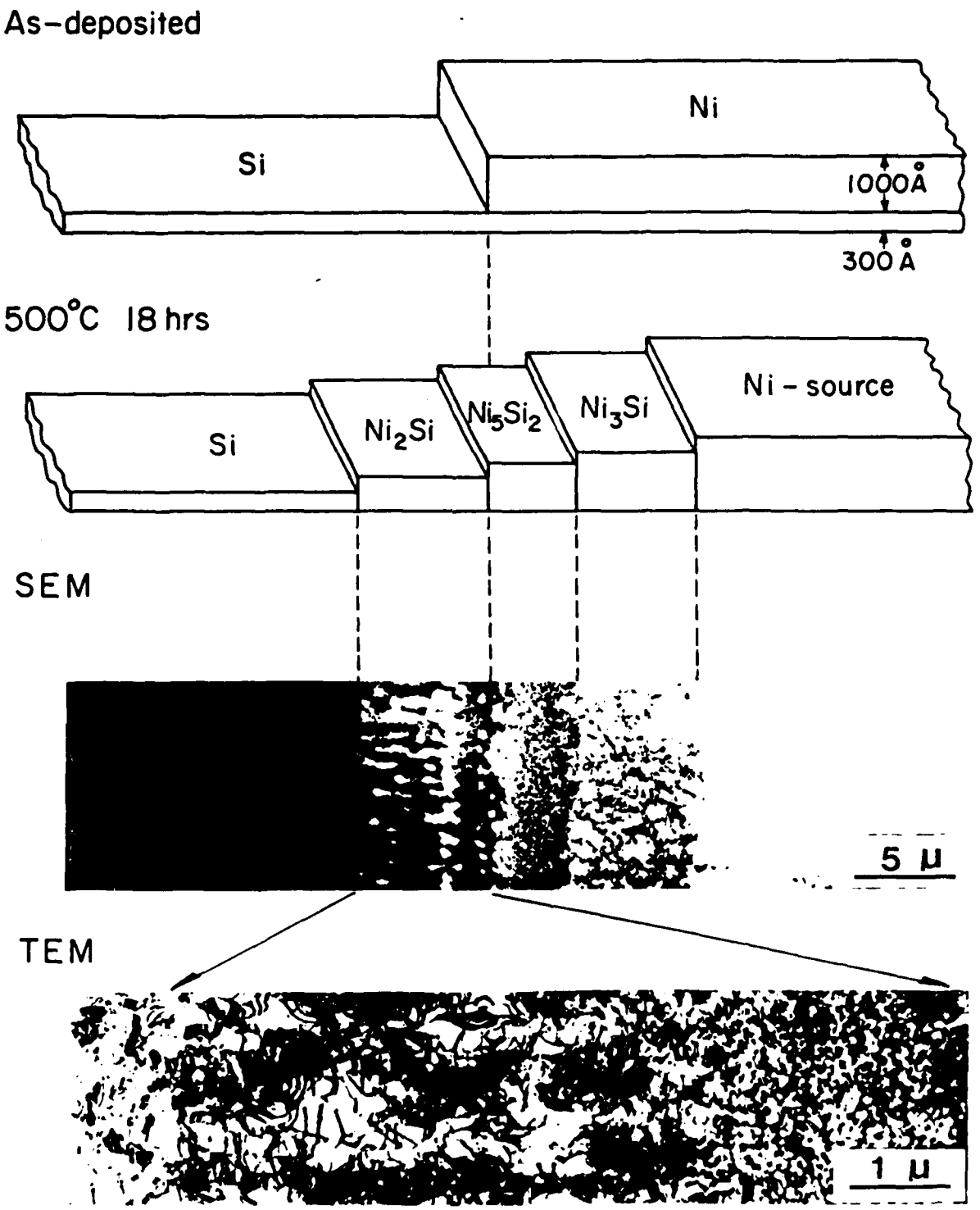



Fig. 2. Ni-Si lateral diffusion couple as viewed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

and composition of the growing silicide phases. We were able to show that the first phase to form was $Ni_2Si$ in agreement with thin film results and that the phase sequence for longer-time or higher-temperature anneals agreed with bulk data. However the lateral resolution was poor as shown in figure 2 for the SEM viewgraph.

The striking improvement in lateral resolution afforded by self-supporting couples with transmission electron microscopy is shown in the TEM viewgraph at the bottom of figure 2. This self-supporting sample geometry - developed as part of the ONR program - was made by depositing Si films and Ni islands on NaCl substrates which were then dissolved in water. The thin films were then mounted on TEM grids for subsequent thermal annealing and electron microscopy analysis.

One of the objectives - which lasted throughout the program and still continues was to show that these self-supporting silicide couples did indeed follow the growth kinetic behavior expected from conventional thin film studies. The growth of the phases followed diffusion-limited growth with silicide length, $L_D$, proportional to the square root of time, t. The growth rate, $L^2/t$, is plotted in figure 3 for the three near-noble silicides, Ni-, Pd-, and Pt-silicide. All three have growth rates and activation energies that agree with the thin-film results - the shaded portions in figure 3.

These results show that self-supporting structures are valid models of both thin-film and bulk behavior. In fact, the lateral couples provide the bridge between thin-films and bulk samples. Consequently we used self-supporting couples as the mainstay of our work in this program. As the program developed on we gained confidence in high spatial resolution electron beam analysis, we did utilize cross-sectional TEM techniques to investigate specific interface structures. However, such cross-section structures destroy the sample and are not suited for the kinetic studies of phase growth that are the underpinning for this ONR project.

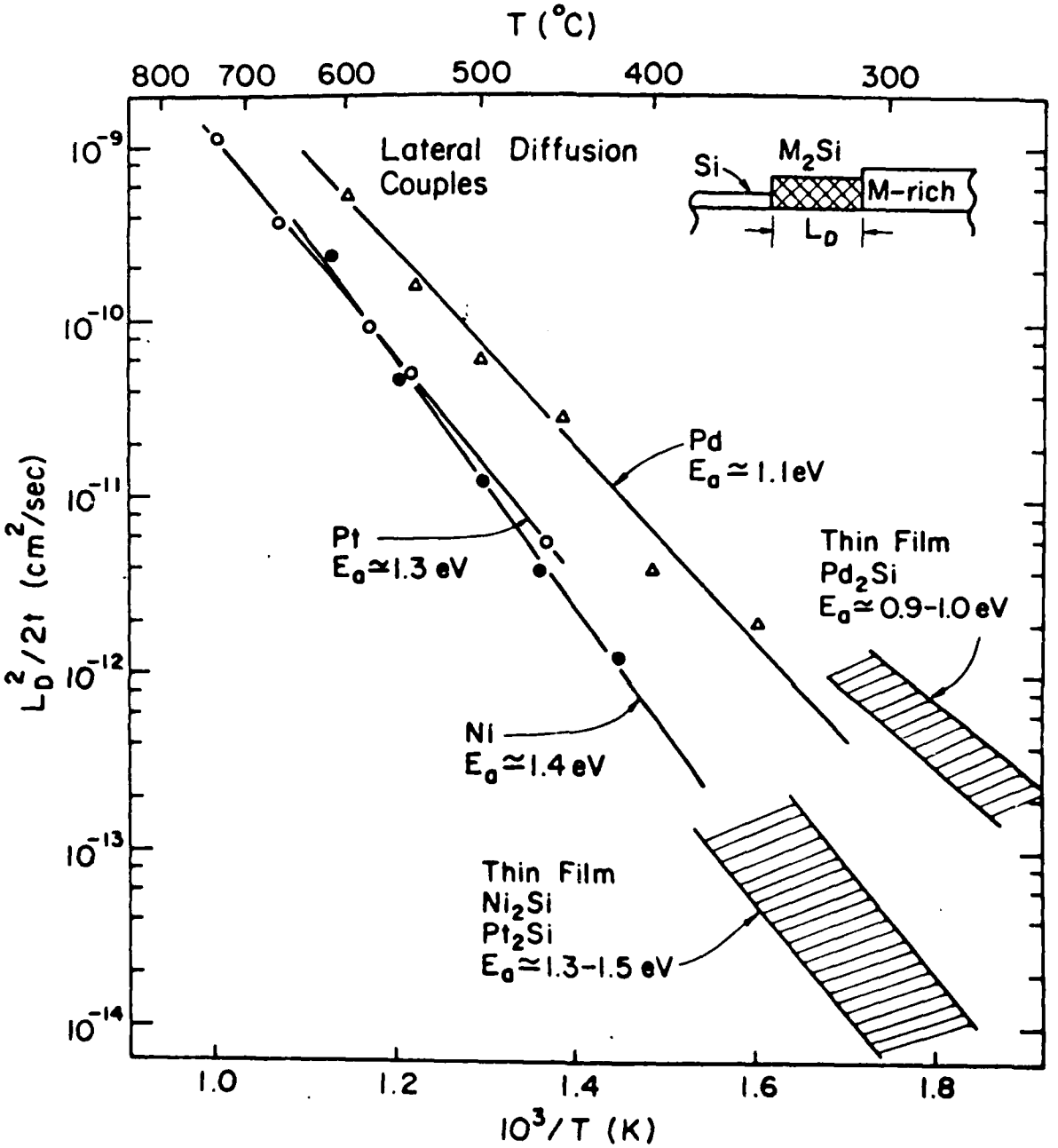



Fig. 3. Growth rate vs. 1/T for Ni, Pd and Pt-silicide lateral diffusion couples. Shaded portion represents conventional thin-film growth rates.

II. Results in relation to "Statement of Work".

The proposal from Cornell dated 13 April 1984 was the basis for the contract award N00014-84-K-0342. The statement of work is quoted here and a brief summary is given after each section. Publication numbers refer to the list of publications acknowledging ONR support given in Section IV.

"1.) In the initial phase of the program we will carry out electron energy loss measurements to measure core-level, interband and plasmon transitions on large area, silicide layers about 500 Å thick. These measurements will be carried out on crystalline and amorphous layers that have been characterized by electron diffraction techniques. The work will emphasize the near-noble metal silicides."

Results: These measurements were carried out (see Publ. Nos. 1 and 2 and figures 4 and 5). Calibration of electron-induced x-ray yields were also made (Publ. No. 4).

"2.) We will then form lateral structures to investigate the silicide/Si interface region using a fine-focus beam. The first sample configuration will be deposited metal and Si layers in structures similar to those used to study silicide formation kinetics. Then we plan to use cross-section TEM samples that have been prepared from fine line silicides formed in oxide windows on a silicon wafer."

Results: These measurements were carried out and formed the basis of the major portion of this program (see Publ. Nos. 3, 5, 11 and 12 and figure 6 for data on silicides and Publ. Nos. 13 and 14 for misfit dislocation analysis at interfaces).

"3.) We intend to study silicide formation in VLSI structures by forming arrays of small area structures. These arrays will be patterned in 2 x 2 mm fields and will be investigated with Rutherford backscattering, glancing angle x-ray diffraction and Auger electron spectroscopy for comparison with unconfined silicide formation in adjacent large-area

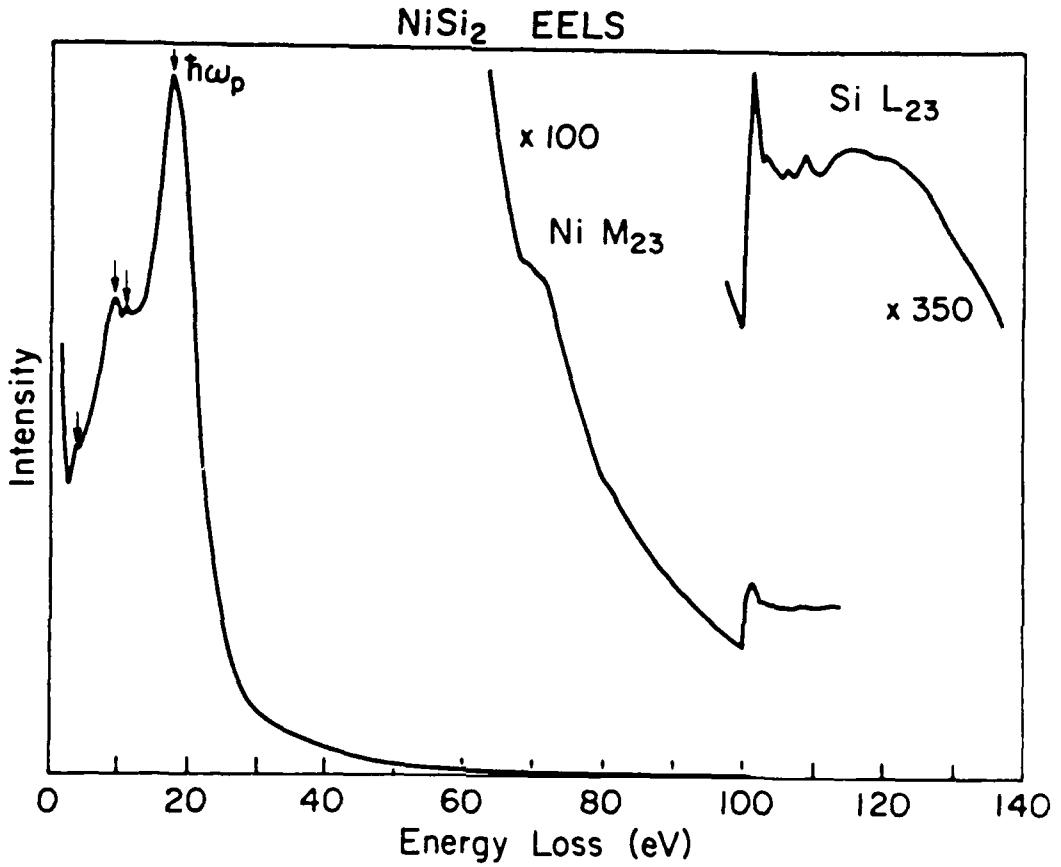



Fig. 4. EELS spectrum of $NiSi_2$ showing characteristic Ni $M_{23}$ and Si $L_{23}$ core level excitations. $h\omega_p$ is the bulk plasmon energy. (Intensity is in arbitrary units.)

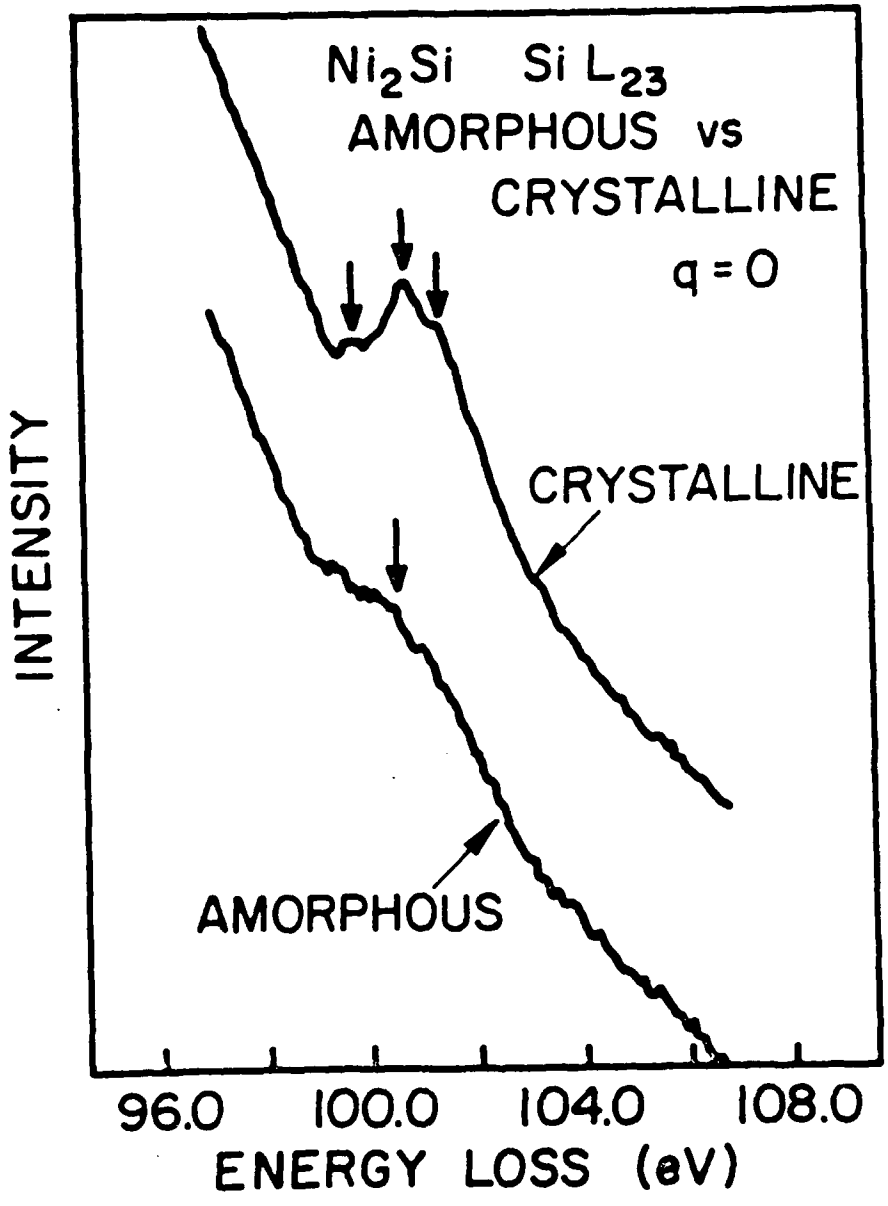



Fig.5. Irradiation dampens the Si $L_{23}$ peaks of $Ni_2Si$, implying the Si derived contribution to the conduction-band density of states is weakened.

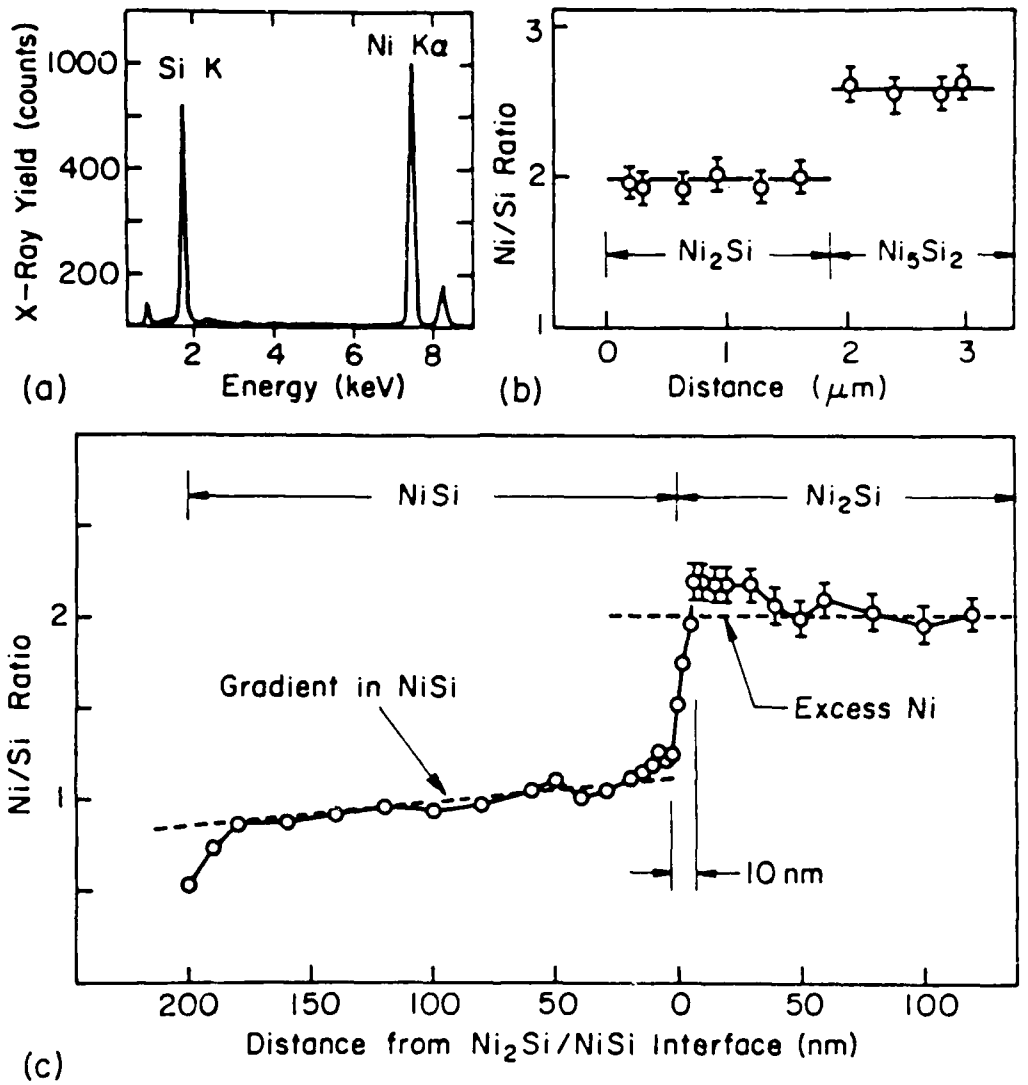



Fig. 6. Energy dispersive X-ray spectroscopy was used to measure the composition profiles in each phase. The $Ni_2Si$ and $Ni_5Si_2$ phases have constant compositions along their length (top right). Distances in both graphs are measured relative to the NiSi-$Ni_2Si$ interface. A composition gradient (lower graph) was measured in the NiSi phase when the grains were less than 200 nm long. The excess Ni on the $Ni_2Si$ side of the NiSi-$Ni_2Si$ interface is caused by a decrease in the Ni diffusivity from the $Ni_2Si$ to the NiSi phase.

geometries. The silicide arrays will also be examined with electron microscopy."

Results: These measurements were made but the samples were unstable and exhibited severe degradation with non-uniform silicides, edge penetration and void formation (see fig. 7). A proper understanding of fine line structures became a major effort; however since this represented a change in philosophy, the work on this program was directed to investigation of Ni/amorphous alloy interfaces (see Publ. Nos. 8, 9 and 10) and Si/poly Si (see Publ. Nos.6 and 7).

"4.) Impurities accumulate at silicide interfaces. To ensure that interface contamination is minimal we intend to upgrade our vacuum annealing system and our deposition system. We intend to provide a modified target chamber for our second beam line so that auger analysis and sputter sectioning can be monitored in situ with RBS measurements."

Results: The end chamber was modified and the vacuum annealing upgraded. These facilities were used routinely in the work carried out under this contract.

III. High Spatial Resolution Measurements.

The objective of this study is to examine silicide growth and analyze the structural, chemical and electronic properties at silicide/silicide interfaces and silicide/silicon interfaces. The samples used were nickel-silicon self-supporting lateral diffusion couples. This sample configuration was used for the small area analysis because thin specimens are needed over large distances to minimize electron beam spreading and maximize the spatial resolution for composition and electronic structure analysis.

The structure or phase of the silicides formed by lateral diffusion was determined using micro-area diffraction in a JEOL 200cx electron microscope at the Cornell Materials Science Center. the smallest area analyzable with the microdiffraction is about 150 $\mathring{A}$ in diameter. We used the lateral

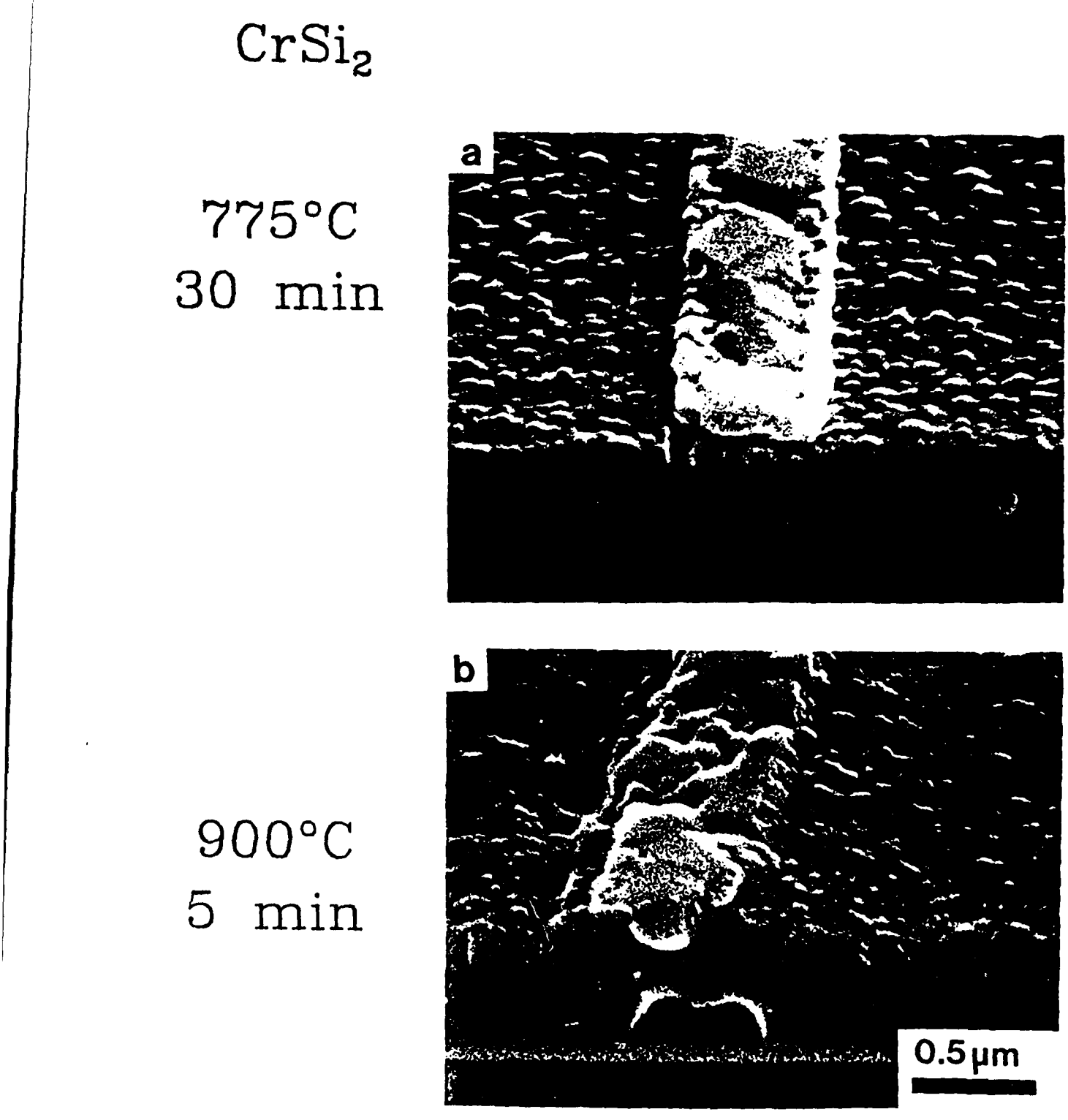



Fig. 7. Degradation of fine-line $CrSi_2$ structures due to thermal annealing.

diffusion couples as an intermediate sample between bulk and thin films, in order to investigate the growth mechanisms in silicide formation.

A VG HB5 scanning transmission electron microscope (STEM) at Cornell was used to probe the NiSi/$Ni_2Si$ interface more closely using energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). The EDS technique can determine compositions to an accuracy of 4.5% and to measure composition gradients across boundaries with an even better accuracy. The concentration within the $Ni_2Si$ and $Ni_5Si_2$ have been measured to be uniform to 4%, and the small area analysis confirms the absence of a phase of composition $Ni_3Si_2$ at the NiSi/$Ni_2Si$ interface.

The counting statistics and energy resolution of the EELS detector on the VG HB5 STEM at Cornell is not good enough to measure the electronic structure from a small area of nickel-silicide. Therefore, we carried out a joint study with P. E. Batson (IBM - T.J. Watson Research Center) using a Wien filter spectrometer on a VG HB5 STEM, to examine the electronic structure of the growing silicides in a lateral diffusion couple (see fig. 6).

This collaboration with Batson was continued (Publ. Nos. 13 and 14) to explore the application of spatially resolved (1 nm) electron-energy-loss scattering to investigate interfaces. This preliminary work has shown that a detailed analysis of accurate, high resolution EELS results will yield information about local bonding and electronic structure. Therefore, a scanning transmission electron microscope, which is optimized for high spatial resolution and angle integrated scattering spectra, is ideally suited for this type of experiment. It is particularly exciting that the defect scattering in the low loss region is very strong relative to the bulk. Thus, EELS may be able to locate single electronic states within structures which have been characterized by high resolution microscopy, to begin the task of relating spatial structure to electronic structure in a fundamental way.

IV. Theses and Publications.

A.) PhD. Theses of Students acknowledging support by ONR (L. Cooper).

1.) John Charles Barbour - January 1986

"The diffusion of Ni in amorphous nickel-zirconium alloys and the composition analysis of nickel-silicide formation in lateral diffusion couples"

("This thesis was made possible by financial support from Larry Cooper of the Office of Naval Research.")

2.) Karen Lynne Kavanagh - May 1987
"Atomic diffusion at poly-crystalline/qallium arsenide interfaces."

B.) Publications acknowledging work supported by ONR (L. Cooper) 1984-1986.

1.) A comparison of electron energy loss spectroscopy and electron diffraction for polycrystalline and Xe irradiated nickel silicides

J.C. Barbour, J.W. Mayer, L.A. Grunes

Thin Films and Interfaces II, J.E.E. Baglin, D. Campbell, W.K. Chu, eds. (North Holland, New York, 1984) pp. 235-240.

2.) An investigation of electron energy loss spectroscopy used for composition analysis of crystalline and amorphous silicides

J.C. Barbour, J.W. Mayer, L.A. Grunes

Ultramicroscopy 14, 79 (1984)

3.) Lateral-diffusion couples studied by transmission electron microscopy

S.H. Chen, L.R. Zheng, J.C. Barbour, E. Zingu, L.S. Hung, C.B. Carter, J.W. Mayer

Materials Letters 2, No. 6A & B, 469-476 (1984)

4.) Calibration of an EDS k-factor using Rutherford backscattering

J.C. Barbour, K. Sickafus and M. Nastasi

J. Vac. Sci. Tech. A3, 1895-1902 (1985)

5.) Silicides and lateral diffusion couples

J.C. Barbour, J.W. Mayer, L.R. Zheng

Inst. Phys. Conf. Ser. 76, 163-171 (1985)

6.) Solid-phase epitaxial regrowth of fine-grain polycrystalline silicon

W. Sinke, F.W. Saris, B.M. Ullrich, J.C. Barbour and J.W. Mayer

MRS Europe, 217-221 (1985)

7.) Solid-phase epitaxial regrowth of fine-grain polycrystalline silicon

W. Sinke, F.W. Saris, J.C. Barbour and J.W. Mayer

J. Mat. Res. 1, 155-161 (1986)

8.) The mobility of Ni versus Zr in an amorphous Ni-Zr alloy

J.C. Barbour, M. Nastasi and J.W. Mayer

Appl. Phys. Lett. 48, 517-519 (1986)

9.) The diffusivity of Ni in an amorphous Ni-Zr alloy

J.C. Barbour

Phys. Rev. Lett. 55, 2872-2875 (1985)

10.) Amorphous Ni-Zr phase formation in self-supporting thin-film lateral diffusion couples

J.C. Barbour and J.W. Mayer

Mat. Res. Soc. Symp. Proc. 57, (1986)

11.) High spatial-resolution analysis of lateral silicide formation

J.C. Barbour, P.E. Batson and J.W. Mayer

Mat. Res. Soc. Symp. Proc. 54, 29-35 (1986)

12.) Silicides and lateral diffusion couples

J.C. Barbour, J.W. Mayer and L.R. Zheng

Microscopy of Semiconducting Materials 1985, A.G. Cullis and D.B. Holt, eds. (Adam Hilgar Ltd., Bristol, England, 1985), p. 163

13.) First observation of interband absorption with a single misfit dislocation at the GaAs/GaInAs interface

P.E. Batson, K.L. Kavanagh, J.M. Woodall and J.W. Mayer

Phys. Rev. Lett. 57, 2729 (1986)

14.) Local bonding and electronic structure obtained from electron energy loss scattering

P.E. Batson, C.Y. Wong, J.M. Woodall and K.L. Kavanagh

Ultramicroscopy (accepted)

15.) Cathodoluminescence of InGaAs-GaAs single heterostructures

E.A. Fitzgerald, K.L. Kavanagh, D.G. Ast, P.D. Kirchner, G.D. Pettit, J.M. Woodall

Mat. Res. Soc. Symp. Proc. 77 (to be published)

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